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MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (STINFO)

24 April 2002

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2002-087**
Brent Viers (PRSM), "Thin Film Properties of POSS"

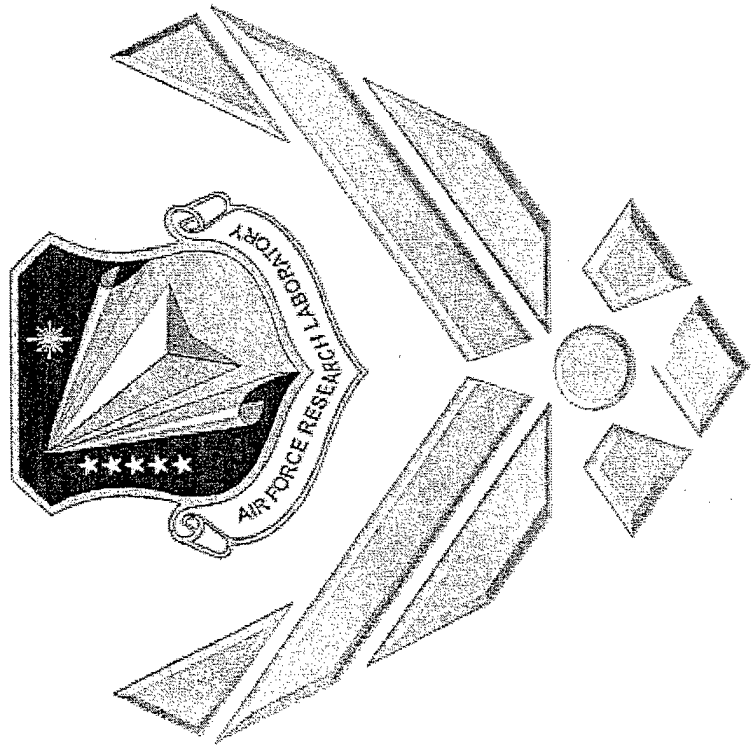
SAMPE Presentation

(Statement A)

(Long Beach, CA, 10-16 May 2002) (Deadline: 16 May 2002)

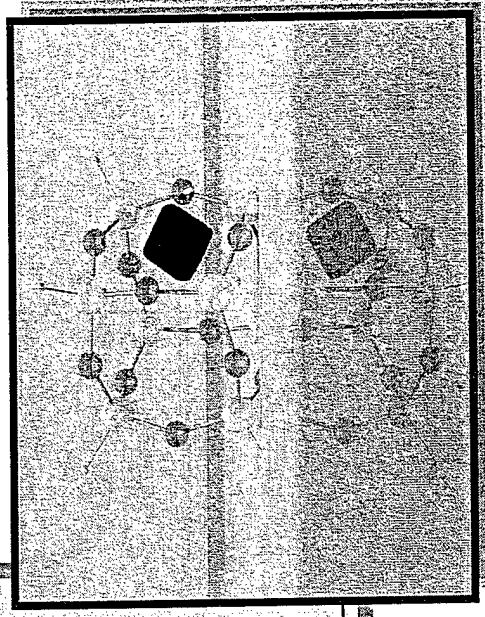
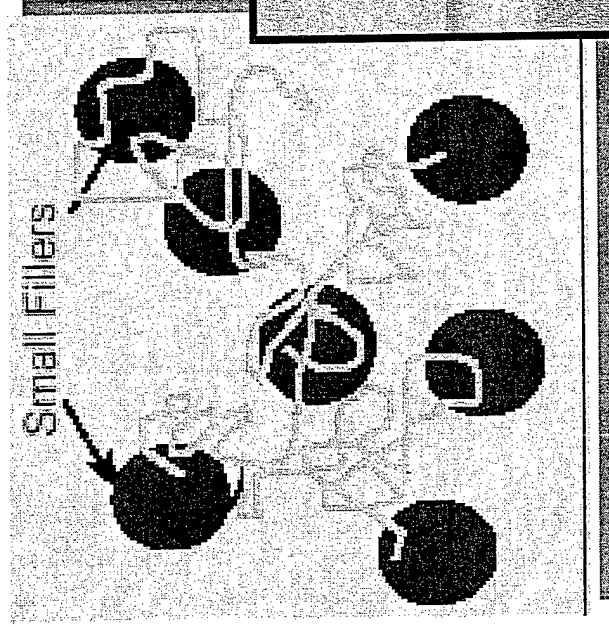
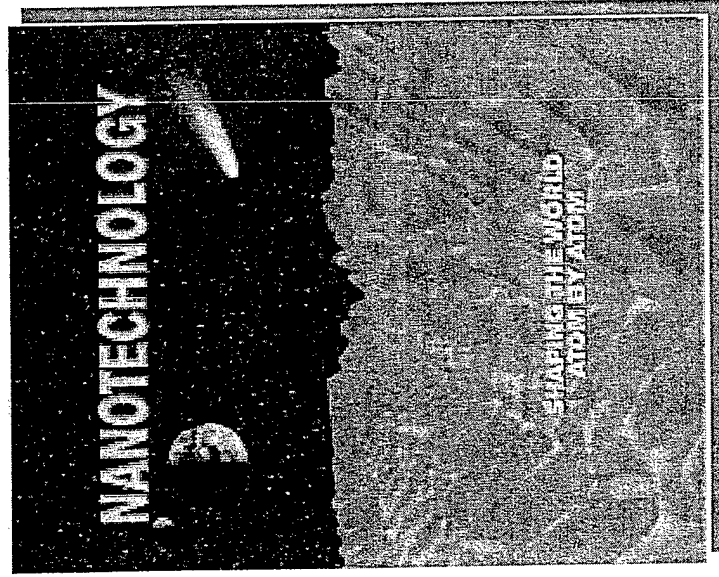
Thin Film Properties of POSS

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited



Dr. Brent Viers
POSS Polymer Group Leader
Air Force Research Laboratory
Propulsion Materials (AFRL/PRSM)
Brent.viers@edwards.af.mil

Inorganic-Organic Hybrids = Nanotechnology



“Perpetual Plastics: By adorning the polymer structure of synthetic plastic with ceramic nanoparticles, researchers hope to develop new substances that will last far longer”

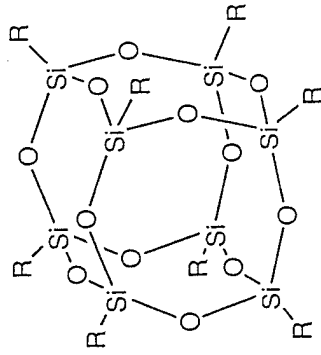
National Nanotechnology Initiative

<http://www.nano.gov>

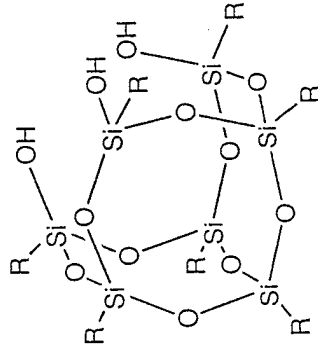
Mark Gordon, Iowa State U

What is POSS?

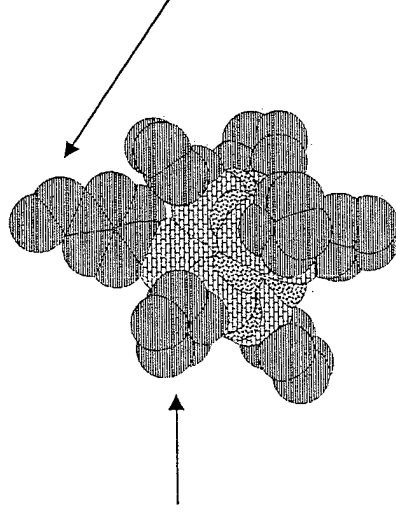
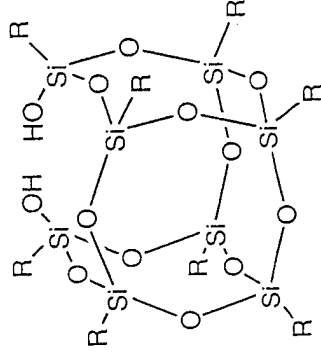
POSS=polyhedral oligomeric silsesquioxane



**Nonreactive organic (R)
groups for solubilization
and compatibilization.**



**May possess one or more
functional groups suitable for
polymerization or grafting.**

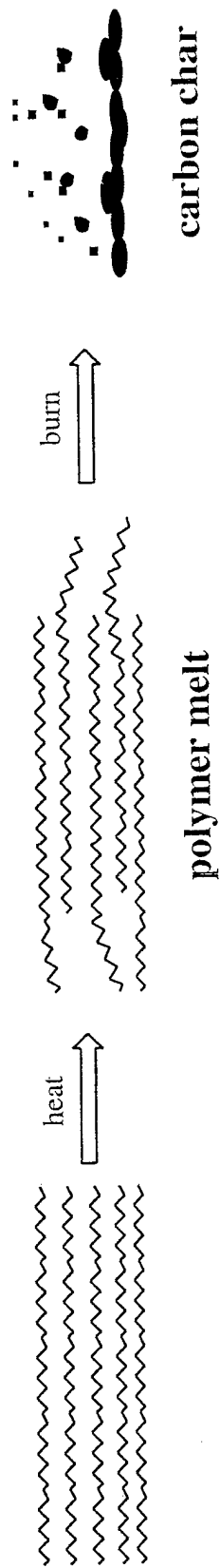


$$\text{Si} - \text{Si} = 5.4 \text{ \AA}$$

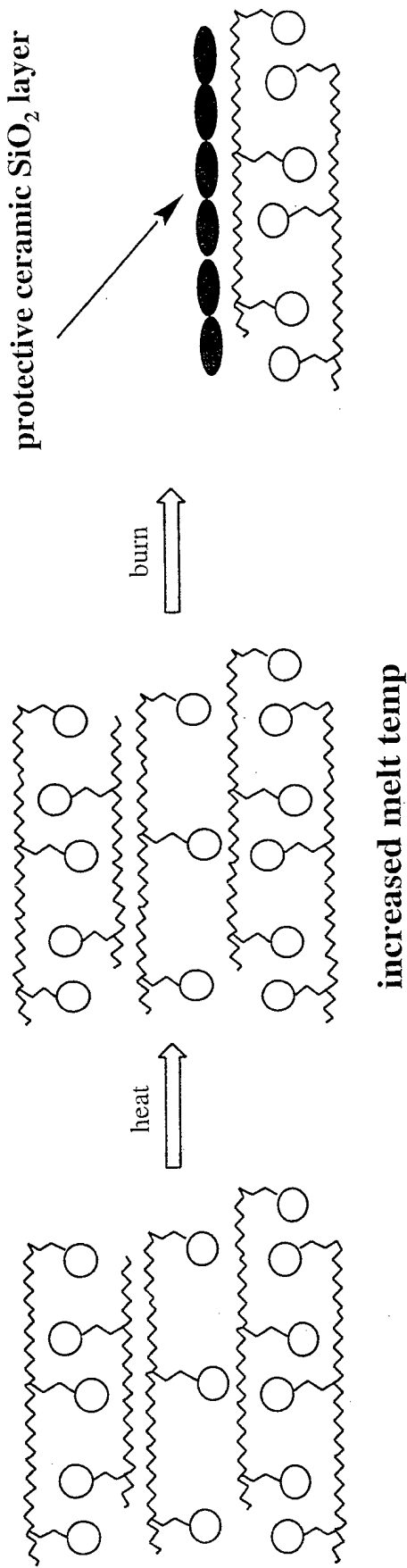
$$\text{Cp} - \text{Cp} = 15 \text{ \AA}$$

POSS for Low Ablation Materials

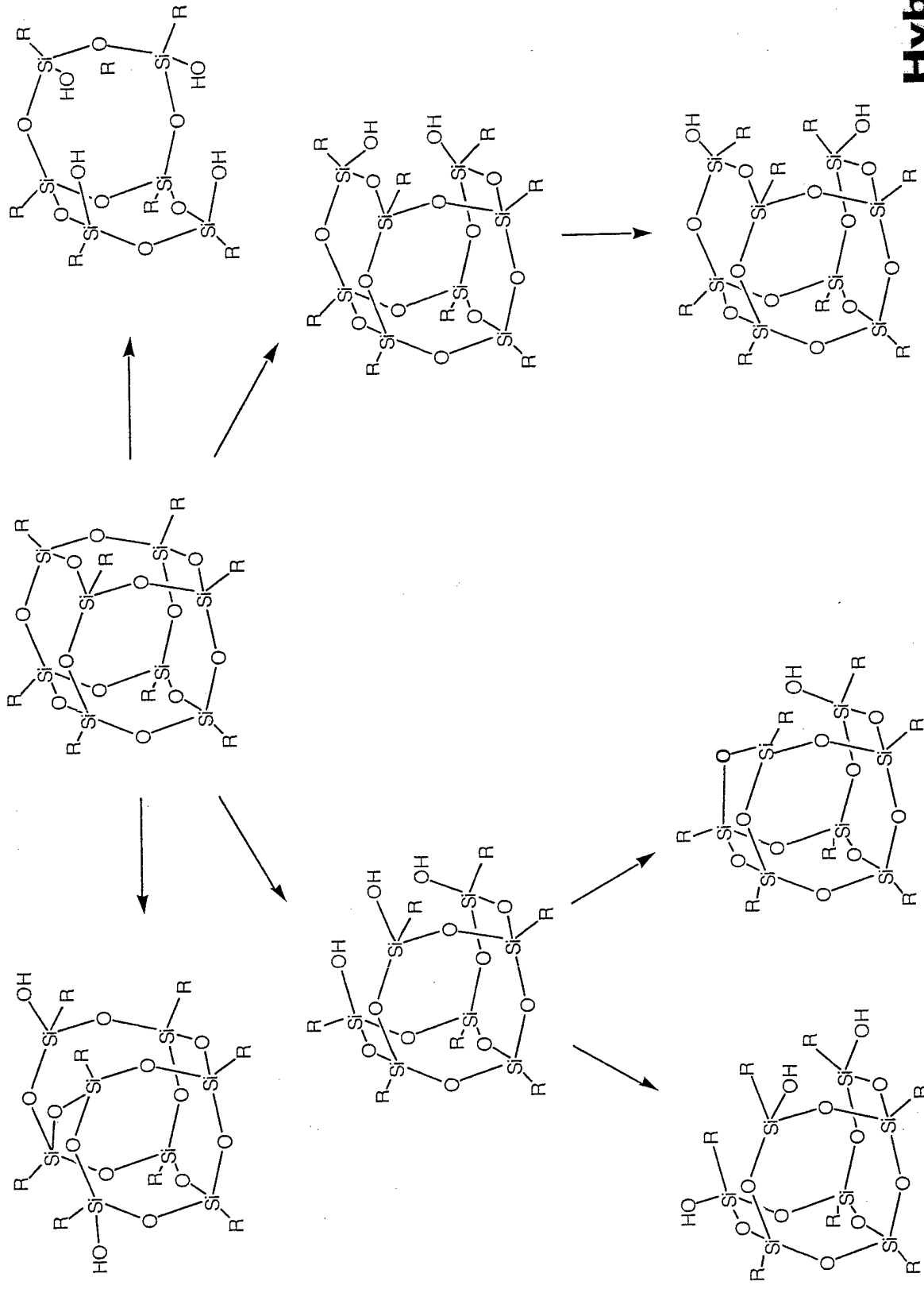
Traditional Polymer



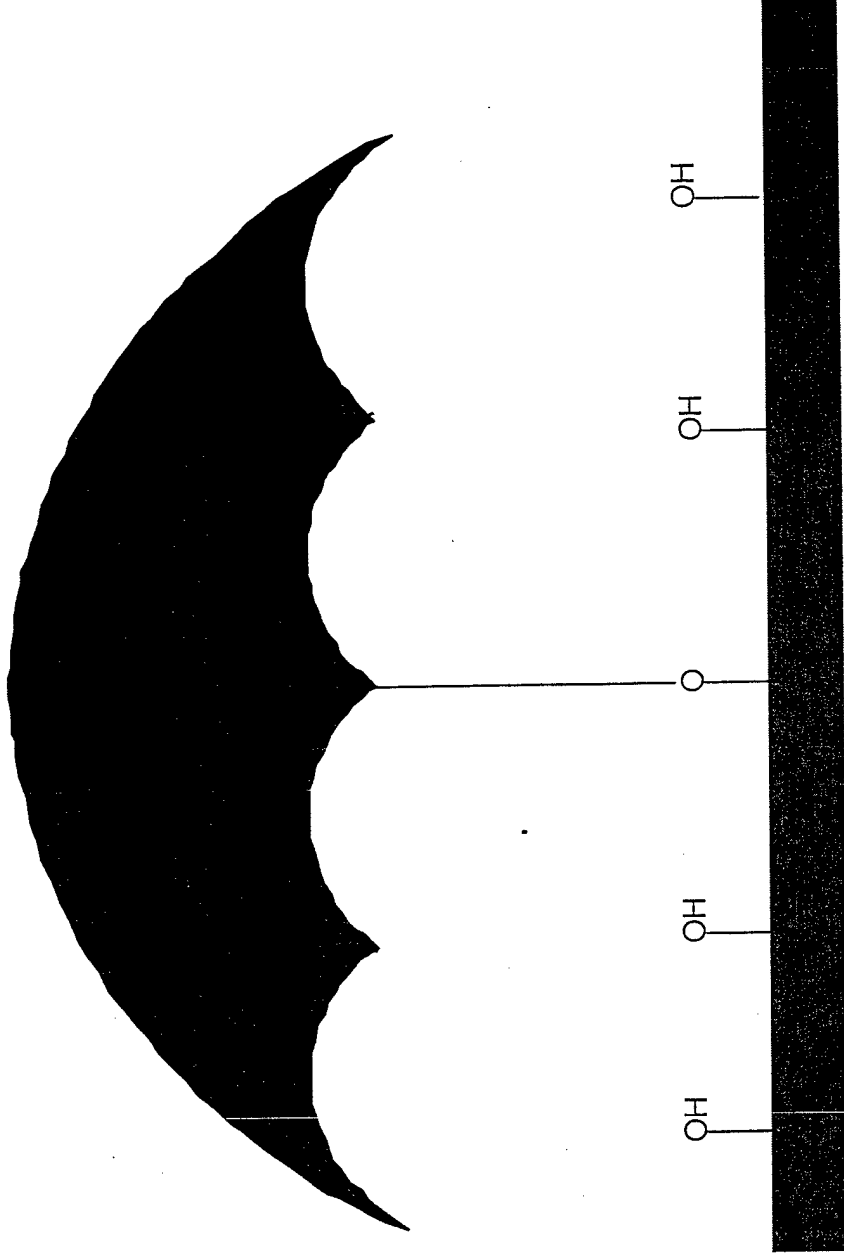
POSS Polymer



Stereochemical and Topological Control

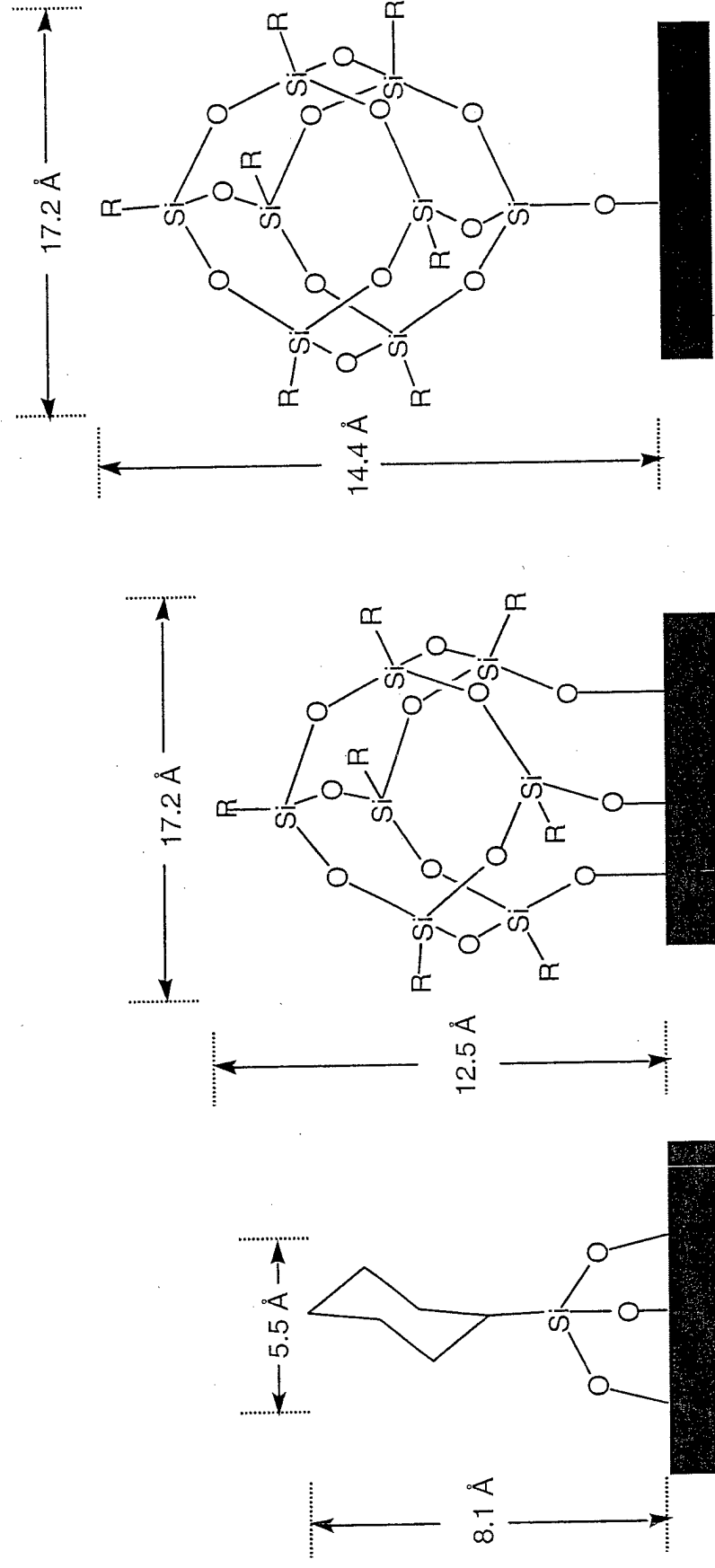


POSSTM: The Hydrophobic “Umbrella”



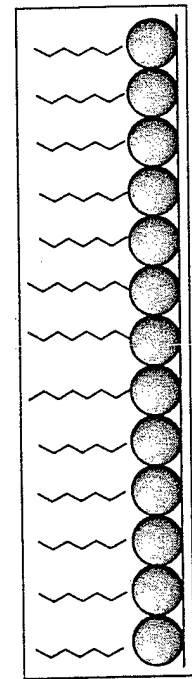
- POSSTM acts as a hydrophobic “umbrella” covering surface Si–OH groups (Approx. 10-12 Si–OH groups/POSSTM nanostructure)
- The surface coverage provided by a single POSSTM cage is approximately 8-10X that provided by a typical silane. (2.32 nm² vs. 0.24 nm²)

Silanes vs. POSS™: Monolayer Comparison



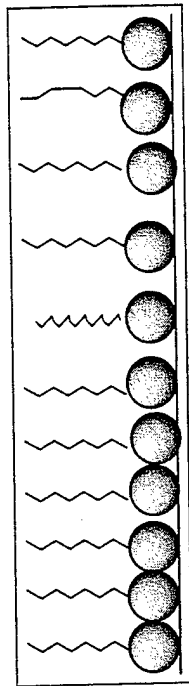
- The well-defined polyhedral structure leads to a more well-ordered, regular surface.
- POSS™ cages provide increased surface coverage leading to a more hydrophobic surface.

States of Monolayer Films



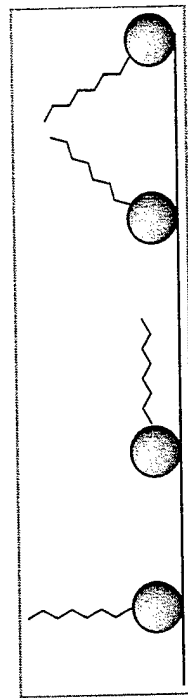
Solid Phase

low compressibility (S), nearly linear plot



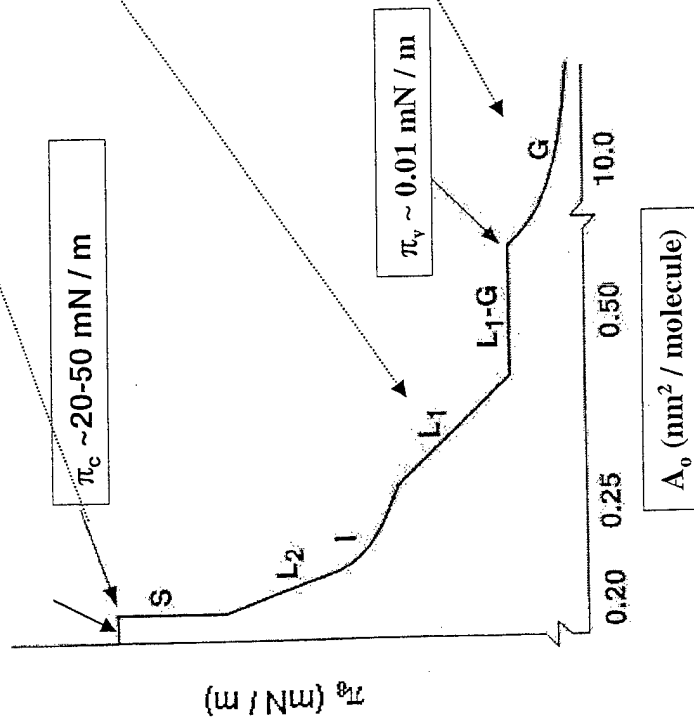
Liquid Phase

appear as liquid, some disorder in the structure, 2 types- liquid expanded (L_1) and liquid condensed (L_2)

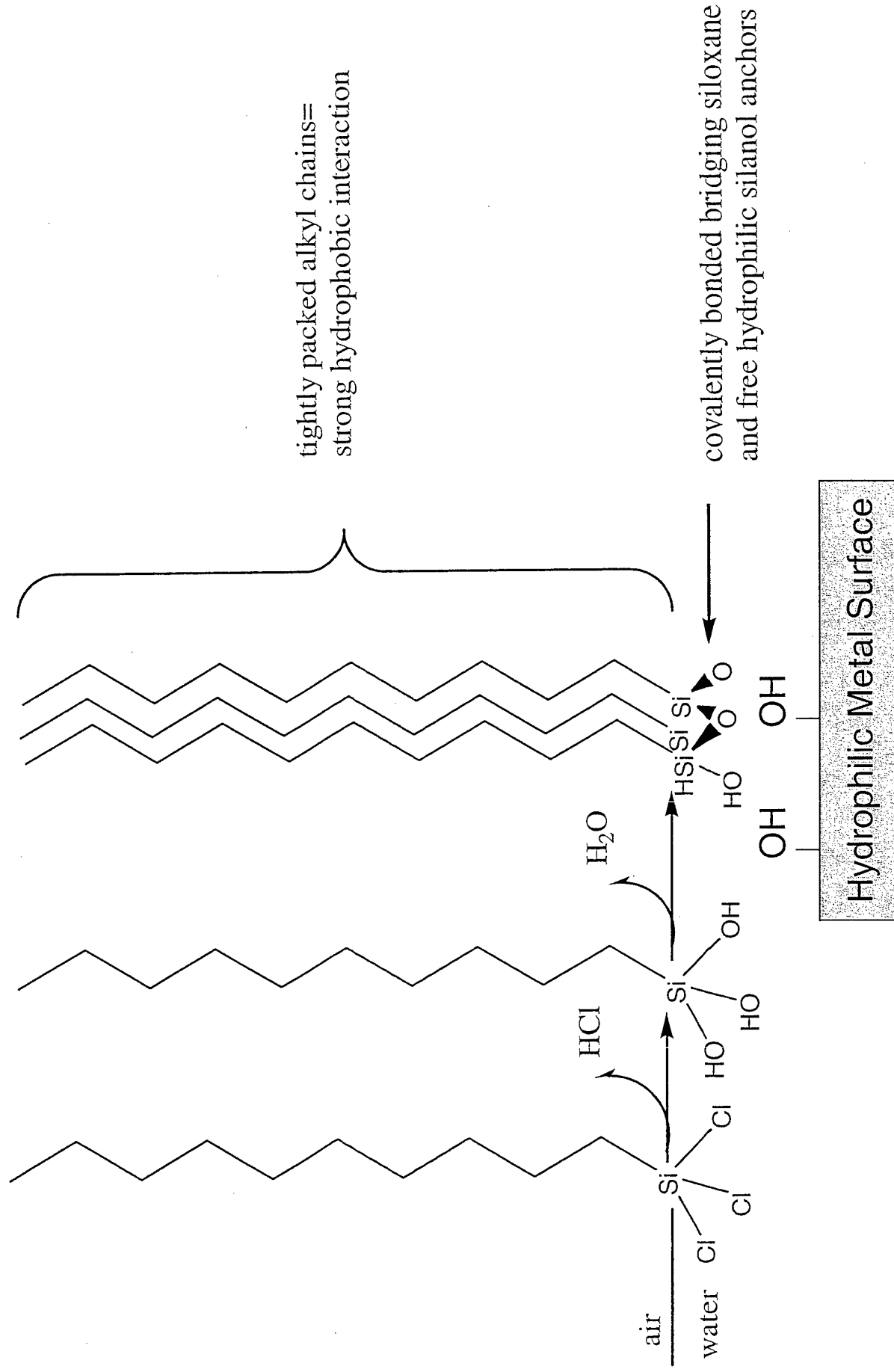


Gas Phase

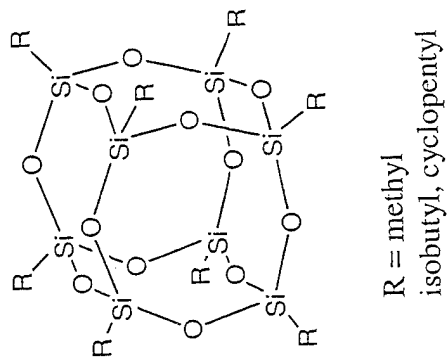
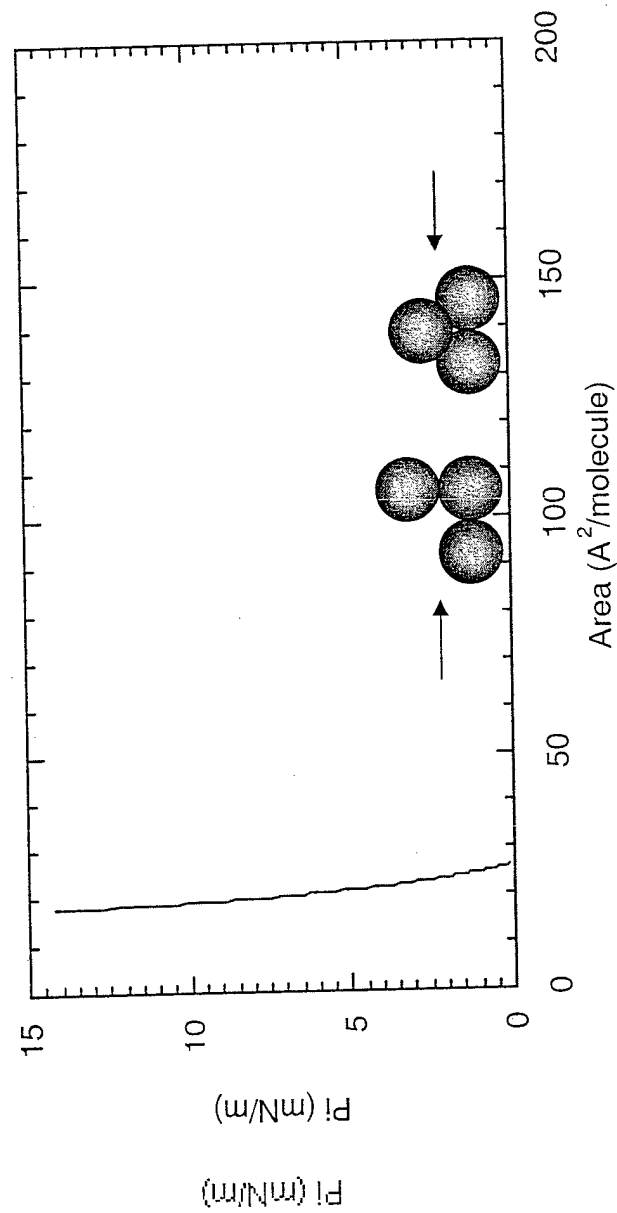
obey an equation of state, Π area per molecule is large, Π as low as 0.001 mN/m



Chlorosilane Self Assembled Monolayers

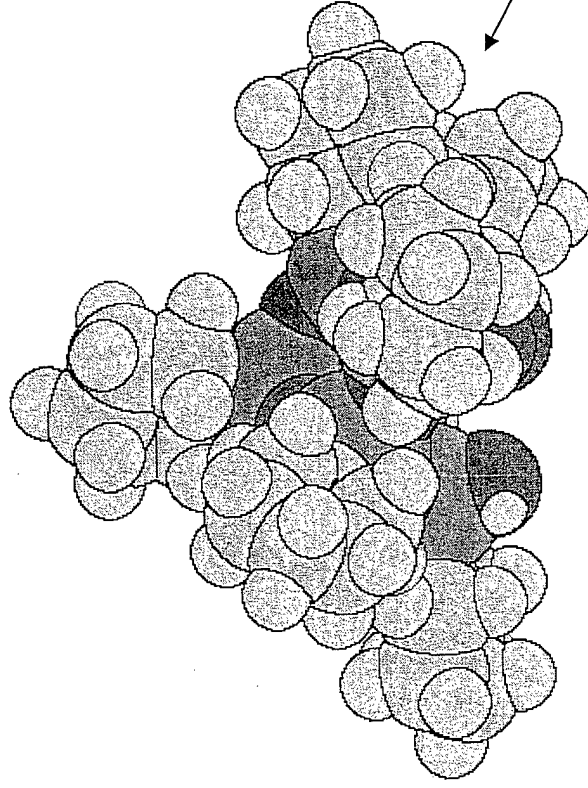


Fully Condensed POSS Cubes



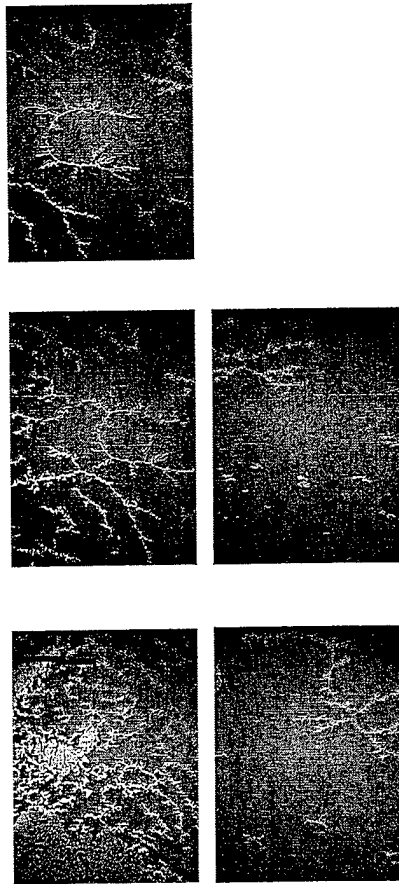
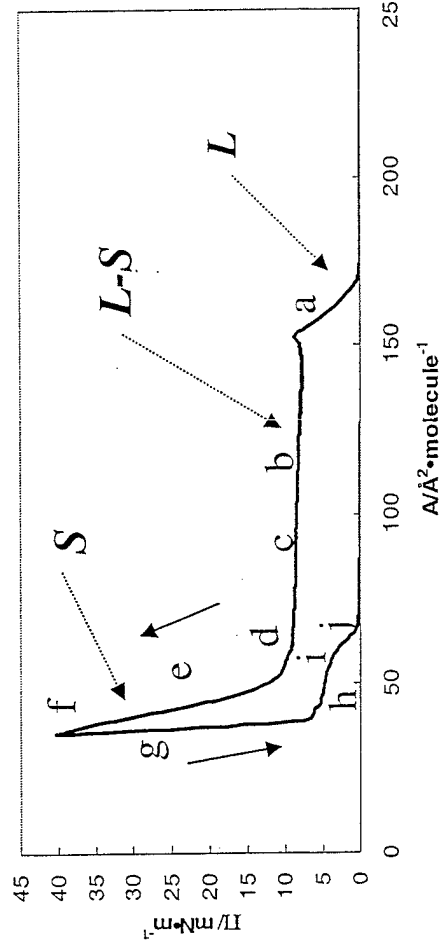
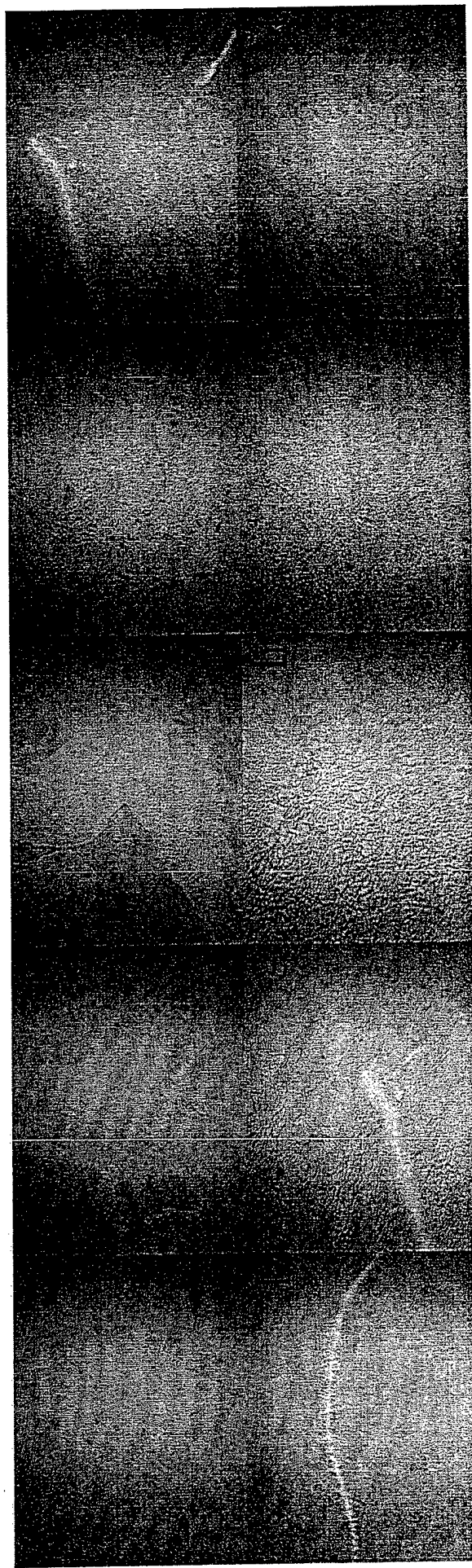
POSS likely exists as aggregates that agglomerate upon compression

Steric Hindrance of POSS



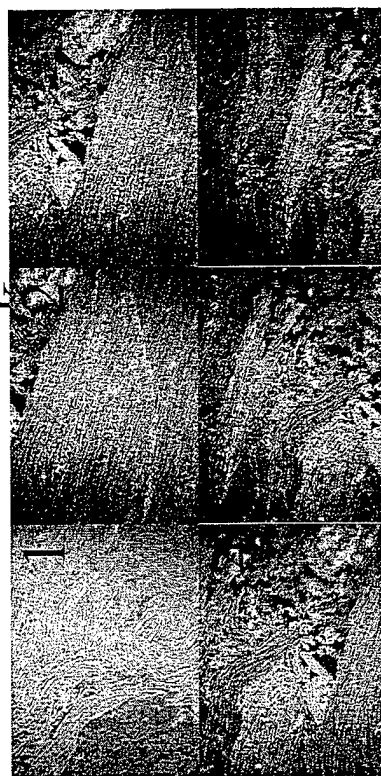
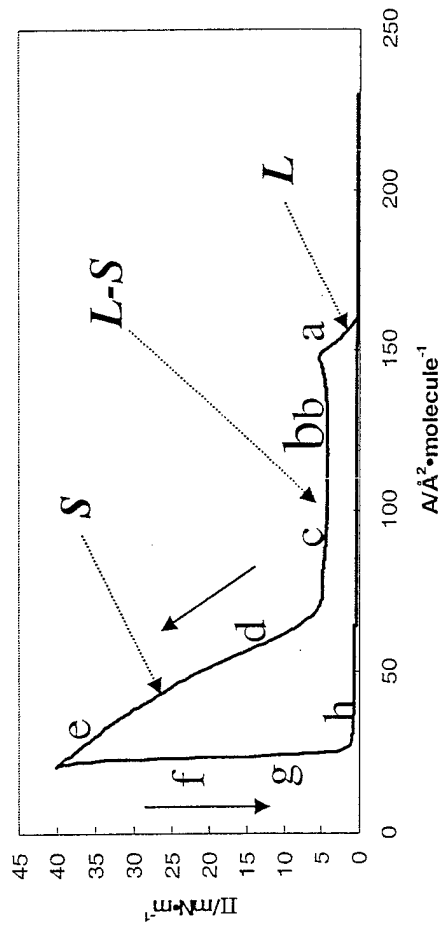
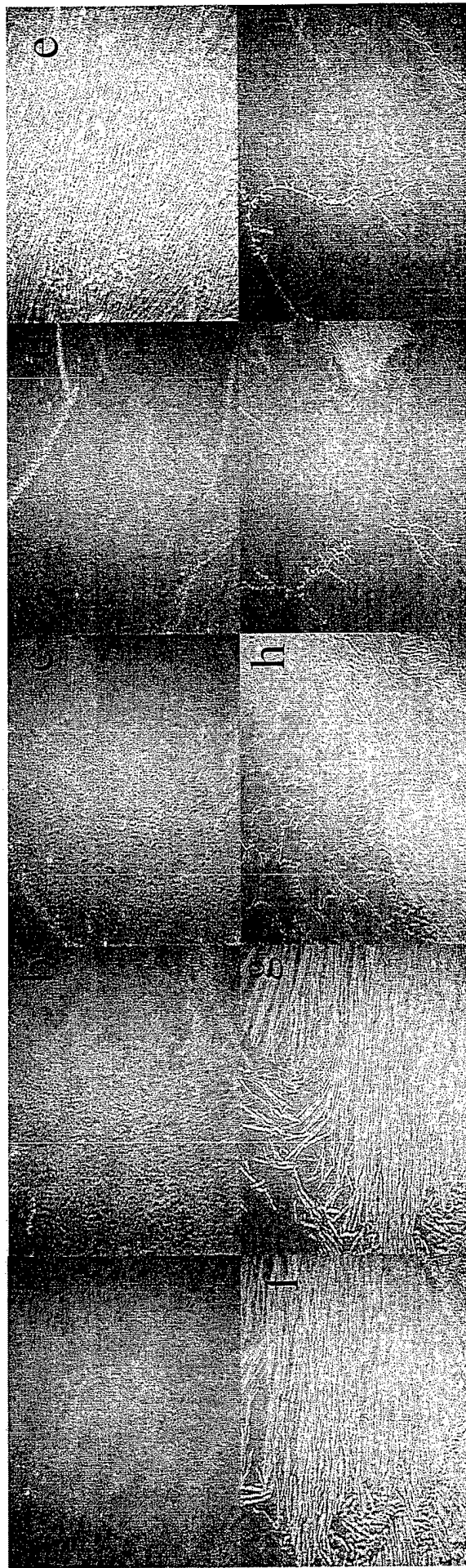
Hydrophobic
Organic groups
Extend past
Hydrophilic
Silanols!

Cyclopentyltrisilanol-POSS @ 22.5 °C



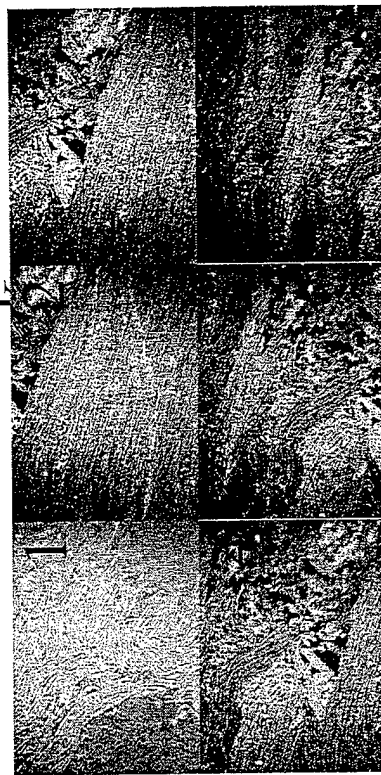
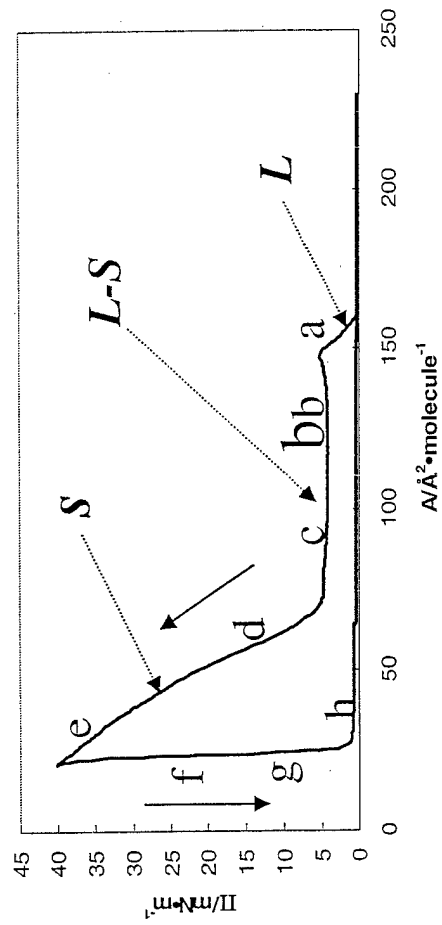
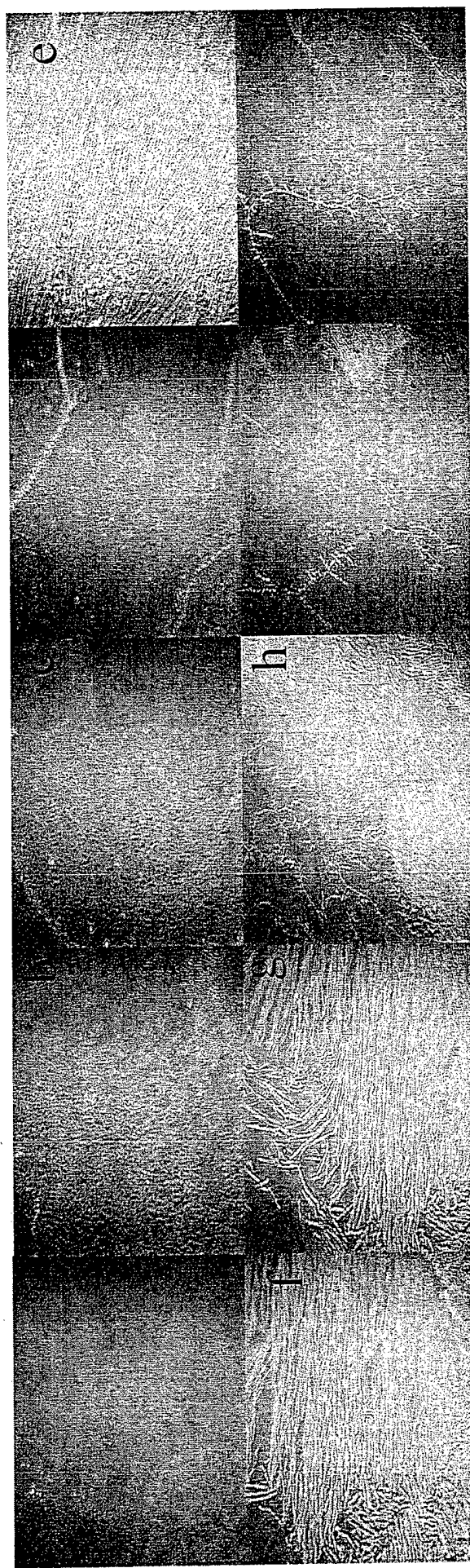
250 1-6 ,dendritic structures obtained during expansion in a second compression/expansion cycle

Cyclohexyltrisilanol-POSS @ 22.5°C



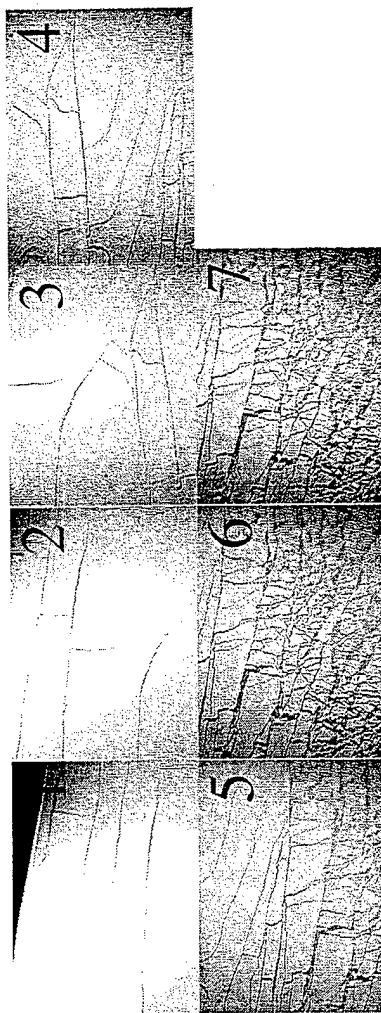
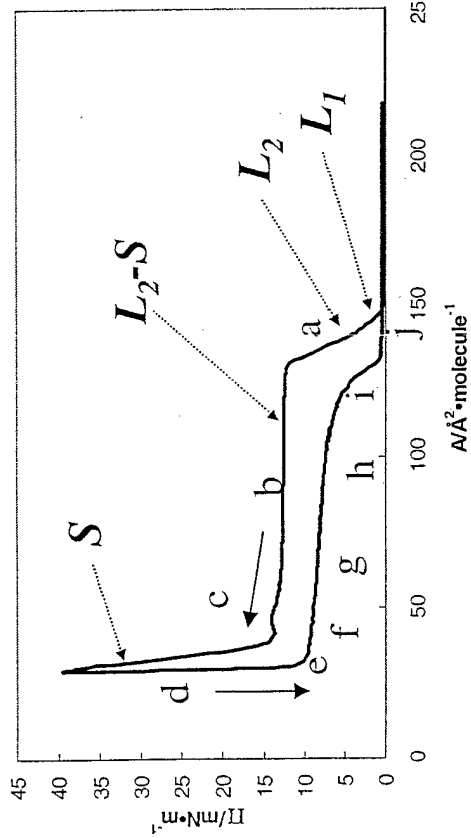
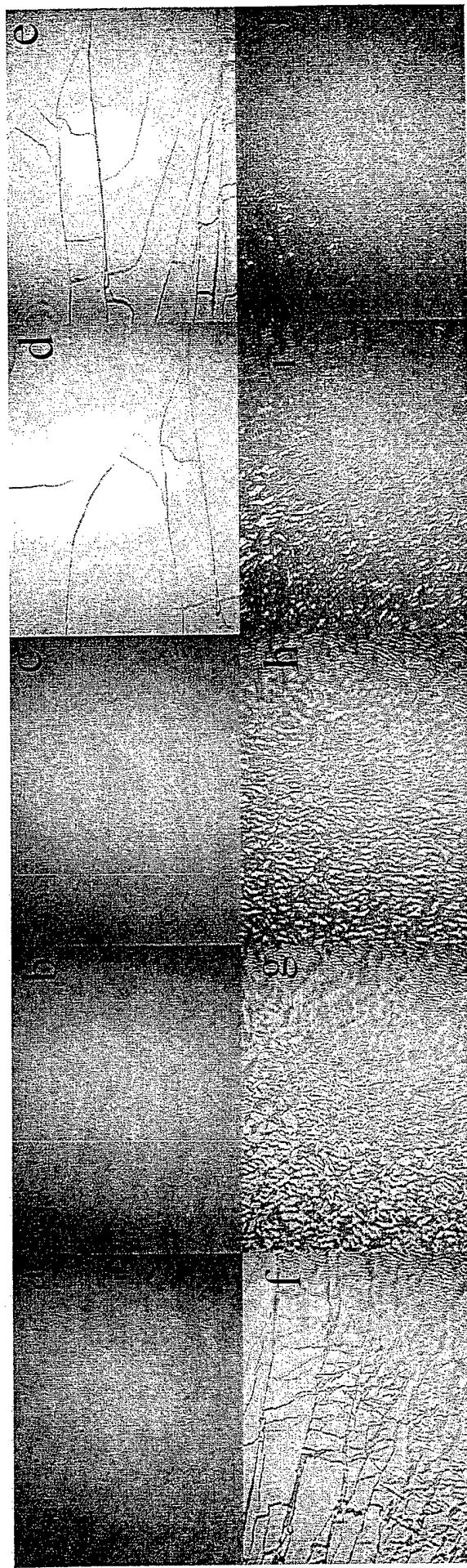
1-6 show the solid state film during 2nd compression

Cyclohexyltrisilanol-POSS @ 22.5°C



1-6 show the solid state film during 2nd compression

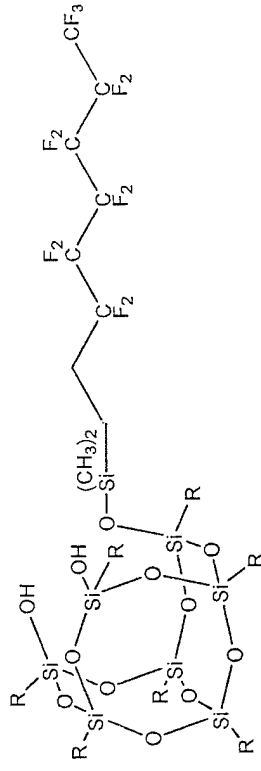
Phenyltrisilanol-POSS @ 22.5°C



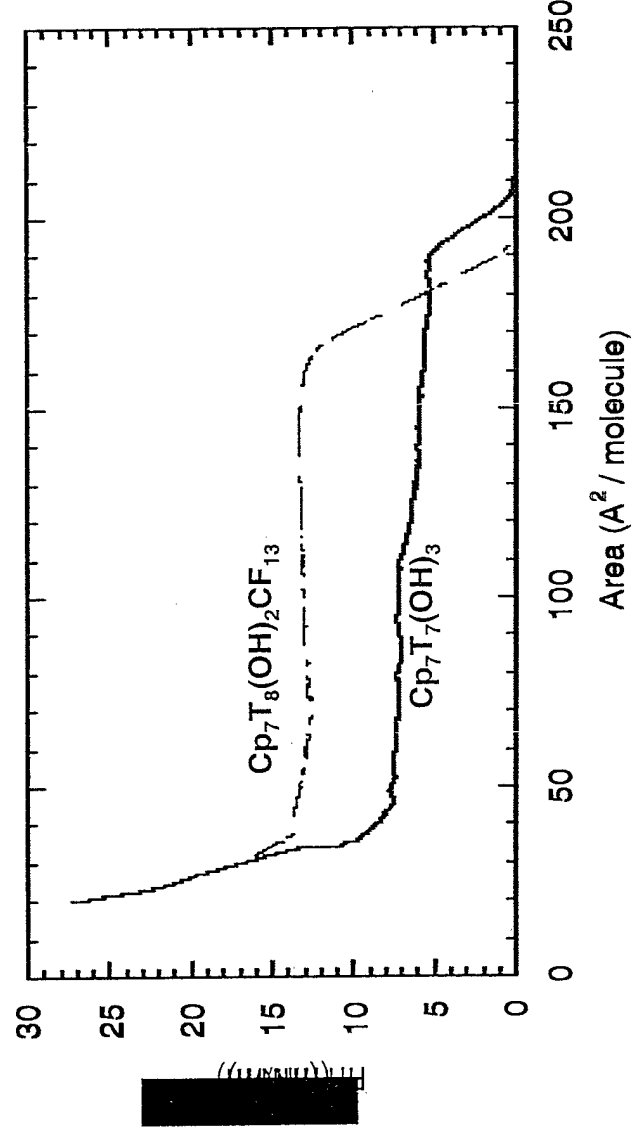
1-7 show the early details of solid state film break-up upon expansion

POSS in a "traditional" surfactant

Quantitative substitution of first silanol



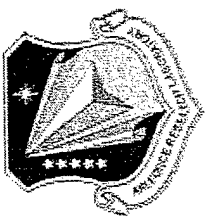
R = cyclopentyl



Pressure-Area behavior is very similar to POSS precursor

Conclusions

- POSS with hydrophilic silanol groups can spread to form monolayers on a water surface
- Different POSS geometries (functionality) can change the compression behavior in a Langmuir Blodgett apparatus
- POSS surfactants can have complicated collapse behavior which likely affects the filler behavior (vis a vis aggregation effects)
- Transfer experiments are underway



Acknowledgments

- POSS group at AFRL-Edwards (Shawn Phillips, Rusty Blanski, Tim Haddad, Brian Moore, Justin Leland, Pat Ruth, Capt. Rene Gonzalez, Maj. Steve Svejda)
- Hybrid plastics (Joe Lichtenhan, Joe Schwab, Bill Reinerth)
- AFOSR (Dr. Charles Lee), Edwards AFRL-
propulsion directorate